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OPTIMIZING THE WELDING OF PLASTICS WITH THE USE OF DIFFERENTIAL SCANNING CALORIMETRY AND THERMOGRAVIMETRIC ANALYSIS

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Abstract. Plastics have different thermal stability, depending on the structure of the polymer chains. It is therefore very important to know their thermal properties, which influence the temperature regime of processing equipment. This paper presents examples of differential scanning analysis (DSC) and thermogravimetry analysis (TG) of selected plastics in an Ar protective atmosphere and also in an oxidative atmosphere of static air. These analyses can be used for proposing a welding temperature regime.

Keywords: plastics; sep polymers; welding; differential scanning calorimetry; thermogravimetric analysis.

1. Introduction

Plastics offer many distinct advantages, e.g., light weight, good thermal and electrical insulation properties, corrosion resistance, chemical inertness, high strength and dimensional stability, absorption of mechanical shocks, good dyeability, potential for decorative surface effects, and low production costs [1].

Future progress in plastics technology may depend mainly on the same factors that set up the recent fast growth. Some of the main factors include [2]:

- Improved understanding of the characteristics of plastics, especially wider long-term and under combined stresses (that is, under combined mechanical, thermal, and chemical effects).
- Development and utilization of new materials and combinations of materials, especially in reinforced plastics or composites.
- Steady reduction in material costs relative to competing materials, taking advantage of low energy requirements for processing and economies of scale.
- Invention and commercialization of new processes.
- Continued improvement in quality, in part due to further automation and in-line measurement and control.
- Advances in recycling technology to reduce the environmental consequences of wider use of nondegradable materials.

Over the past few years, thermoplastic polymers have been progressively replacing metals in the automotive and aerospace industries, medicine, packaging, electronics, construction, etc. Welding increases the versatility and applicability for thermoplastic polymers. Welding techniques for thermoplastics are divided into three categories[3].

Thermal methods are based on conducting heat to the welding surface. A heat source is placed between the joining surfaces. When the surfaces are melted, the heat source is removed. The surfaces are put into contact under pressure until the weld solidifies [4]. These methods conclude:

(1.) Heated tool welding;

(2.) Hot gas welding;

(3.) Extrusion welding;

(4.) Infrared welding;

(5.) Laser beam welding.

Thermal welding methods have a number of advantages and disadvantages. Heated tool welding and hot gas welding are simple and economic, but they have high requirements on the skills of the operator. Extrusion welding has shorter processing times than heated tool and hot gas welding. The advantages of infrared welding include a short processing time, absence of contact with the welding surfaces and suitability for high temperature thermoplastics. On the other hand, two-step processes and some kinds of thermoplastics absorb infrared radiation. Laser beam welding is based on the absorption of radiation. Some pigments absorb laser radiation, which may influence

the colour of the thermoplastics being welded [3].

Friction methods involve rubbing together with pressure force. These methods include:

(1.) Vibration welding;

(2.) Ultrasonic welding;

(3.) Spin welding;

(4.) Stir welding.

Vibration welding is suitable for parts of relatively high stiffness, and offers the advantages of robust machinery, simple processing without accessories, and minimal polymer degradation [5]. Ultrasonic welding is suitable for joining parts of low strength. It entails greater frequency vibration (up to 40 kHz), and requires better surface preparation than vibration welding [5]. Spin welding is applicable only for symmetrical and circular cross-section components. Friction stir welding (FSW) is technically based on the heat produced by surface friction, which causes intense motion in the molecular structure of the material to be welded. However, an exit hole remains when the tool is removed [3].

Electromagnetic methods contain:

(1.) Resistance;

(2.) Microwave;

(3.) Induction;

(4.) Radiofrequency.

Resistance welding has shown performance and cost benefits over other joining techniques, and is being used in current applications [6]. Microwave welding has several unique benefits, for example short processing time, and usability for complex geometries. The material degradation risk for polymers with polar groups is the main disadvantage [3, 4]. Induction welding has a short process time and is usable for complex geometry but the machinery is quite expensive [3]. Radiofrequency welding is most commonly used. It is a relatively fast process with typical cycle times from less than 2 seconds to 5 seconds. No special joint designs are required [4].

During production, processing and application, plastics are often subjected to temperature-dependent structural changes. Thermal analysis for characterization of plastics is widely practiced in research and industry today [1]. There are three different basic thermal analysis techniques for polymer analysis: differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and thermomechanical analysis (TMA) [2].

DSC instruments are widely used for the thermal characterization of plastics [7]. DSC is a technique that measures the heat flow in or out of a material as a function of time or temperature. The required sample size is relatively small, and very little sample preparation is required. This leads to a fast analysis time. In a DSC measurement, information about thermal and mechanical history (processing influences, crystallinity and curing, service temperature) is revealed by the first heating curve. For a forensic comparison of chemically similar samples, the thermal history plays an important role because subsequent controlled cooling creates a "new" known specimen history, which gives the same characteristic properties to all materials [8]. The advantage of DSC in comparison with other calorimetric techniques lies in the broad dynamic range regarding heating and cooling rates, including isothermal and temperature-modulated operation [9]. DSC is a useful tool for characterizing thermoplastics by determining the glass transition temperatures. This technique is especially useful in characterizing copolymers and blends, where this information may be directly applied to determining the formulation changes required to improve the physical properties [10, 11].

Figure 1. Netzsch STA 409CD — Simultaneous Thermal Analysis Apparatus.

2. Method

Differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements were employed in this study. Both measurements were performed on a Netzsch STA 409CD Simultaneous Thermal Analysis Apparatus (Fig. 1). This instrument is able to record both measured values (DSC and TG) at the same time.

The samples were tested under non-isothermal conditions at the same scanning rates of 10 K/min in two steps: heating and cooling. The temperature range of the measurements was from room temperature to

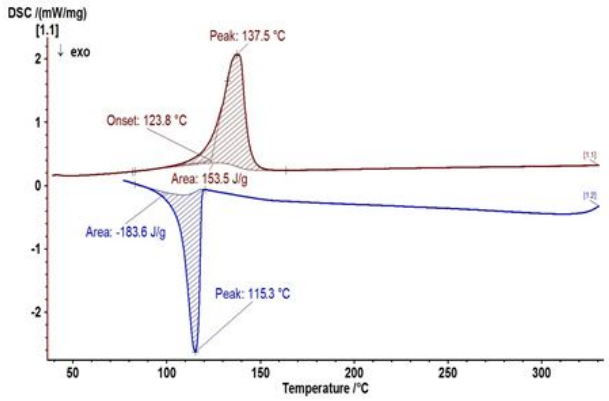

FIGURE 2. DSC-TG record of HDPE (4.5 mg) measured in argon.

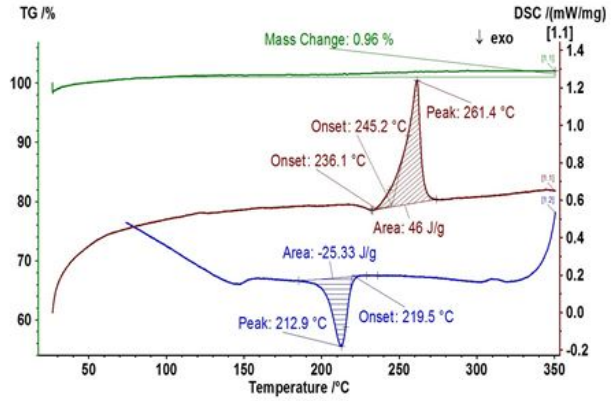

FIGURE 4. DSC-TG record of PA-66 (4.6 mg) measured in argon.

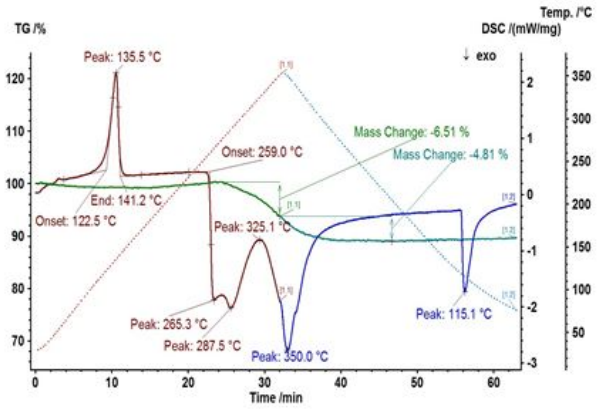

FIGURE 3. DSC-TG record of HDPE (3.8 mg) measured in air.

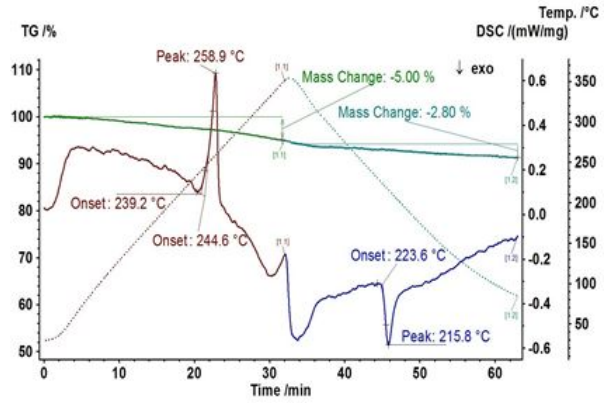

FIGURE 5. DSC-TG record of PA-66 (2.0 mg) measured in air.

350 °C. The specimen, i.e., High Density Polyethylene (HDPE) and Polyamide66 (PA66) was measured in an inert atmosphere and also in an oxidizing atmosphere.

The first measurements were conducted in a protective atmosphere of pure Ar (99.9999 vol.%). A furnace was evacuated and purified by Ar before the measurements. The gas flow of Ar during the measurements was 60 ml/min.

The measurements in an oxidizing atmosphere were conducted in static air in a furnace without active gas flow.

The samples were loaded onto an aluminium pan covered by an aluminium lid. The weight of the samples varied between 3.9 mg and 8.7 mg.

Thermal properties such as glass transition temperature (T_g), melting temperature (T_m) and solidification temperature (T_s) were measured. The thermal stability of the samples was investigated with a TG.

3. Results

The DSC-TG results for the HDPE sample (4.5 mg) tested in Ar protective atmosphere are shown in Fig. 2. The weight of the HDPE sample for the DSC-TG measurement in the static air atmosphere was 3.8 mg. The DCS-TG record (heating and cooling) is shown in Fig. 3. The axes are again in the TG (left), DSC (right) versus the Time coordinates.

Fig. 4 shows the simultaneous DSC-TG measurement of the PA-66 sample (4.6 mg) performed under an Ar protective atmosphere. DSC-TG measurements of the same PA-66 sample, but in an air atmosphere are shown in Fig. 5. The mass of this sample was 2.0 mg.

4. Discussion

The red DSC curve in Fig. 2 (HDPE sample) shows again only the endothermic changes in the sample during heating (10K/min). The sample started to melt at about 100 °C; however the major components of the sample started to melt at a higher temperature of 123.8 °C and the sample was completely melted at 137.5 °C. The specific heat required for melting was 153.5 J/g. The melted sample was stable during further heating. During cooling, an exothermic reaction occurred at 115.3 °C.

Fig. 3 shows that this sample began to melt at 122.5 °C in an air atmosphere. However, at 259 °C, exothermic reactions occurred in at least three steps related to a mass loss of about 11.3 %.

The exothermic reaction representing solidification

at 115.1 °C is shown in the DSC cooling curve. This measurement demonstrates that during heating in an air atmosphere both a melting reaction and an oxidative degradation of the HDPE sample occurred.

The red curve in Fig. 4 represents the DSC signal of the PA-66 sample during heating. Two extrapolated onsets at 236.1 °C and 245.2 °C can be evaluated in the melting peak. The specific heat consumed by melting of the sample was 46 J/g. the blue curve represents the DSC signal during cooling. The extrapolated onset of solidification of the sample was shifted to a lower temperature due to undercooling. The thermogravimetric curve (green) shows a negligible mass change during heating.

The simultaneous DSC-TG record of the PA-66 sample measured in an air atmosphere is plotted against time (Fig. 5). An endo- and exothermic peak related to melting and solidification also appeared during heating (red curve) and cooling (blue curve), respectively. Moreover, the exothermic reaction between 300–350 °C was visible in the heating curve. The total mass loss during the whole measurement was up to 8 %.

5. Conclusions

This paper has demonstrated that simultaneous TG-DSC measurements can be utilized for determining melting temperatures and also for determining thermal degradation in a protective atmosphere and thermal oxidation in an air atmosphere during heating.

The measured values can determine the optimal temperature parameters for plastic welding.

The difference between these two plastics relates to the diversity of their macromolecular structures.

The results of the measurements presented here introduce important parameters for subsequent processing of plastics by welding.

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